

## Tripotassium tris(oxalato- $\kappa^2$ O,O')-aluminate bis(hydrogen peroxide) hydrate, the first example of a cyclic hydrogen-bonded $\text{H}_2\text{O}_2$ dimer

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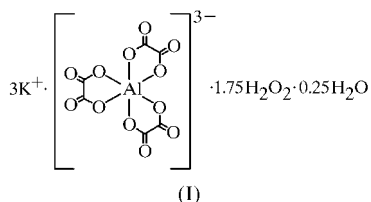
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In addition to associating into cyclic hydrogen-bonded dimers [ $\text{O}\cdots\text{O} = 2.663$  (1) and  $2.914$  (1) Å], each hydrogen peroxide molecule in the title structure,  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]\cdot 1.75\text{H}_2\text{O}_2\cdot 0.25\text{H}_2\text{O}$ , hydrogen bonds to a neighbouring oxalate ligand [ $\text{O}\cdots\text{O} = 2.700$  (1) and  $2.730$  (1) Å] and coordinates to two  $\text{K}^+$  ions [ $\text{K}\cdots\text{O} = 2.6620$  (9)– $2.8380$  (7) Å].

### Comment

Several oxyacid salts form perhydrates on recrystallization from aqueous hydrogen peroxide. These include the commercially important bleaches  $\text{Na}_2\text{CO}_3\cdot 1.5\text{H}_2\text{O}_2$  (sodium percarbonate) (Adams & Pritchard, 1977; Carrondo *et al.*, 1977; Adams *et al.*, 1979) and  $\text{Na}_6(\text{SO}_4)_4\text{Cl}\cdot 2\text{H}_2\text{O}_2$  (Adams *et al.*, 1978, 1981; Adams & Pritchard, 1978).

As the hydrogen peroxide molecules are disordered in the above compounds, accurate geometries for  $\text{H}_2\text{O}_2$  solvate molecules are usually obtained from other perhydrates, notably the alkali metal oxalate monoperhydrates (Table 3). Even in these structures, the hydrogen peroxide geometry is variable, particularly the torsion angle, which adapts to the local environment. The title structure, (I), is the first example

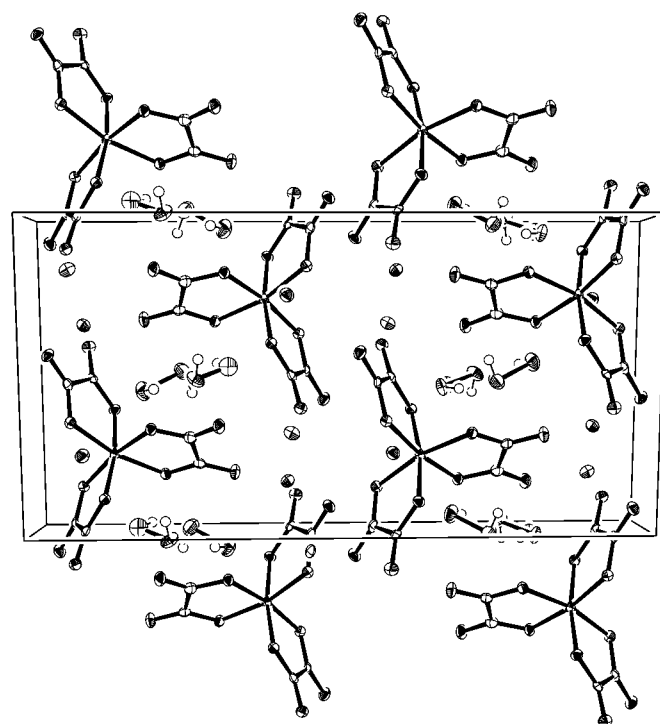


of an oxalate perhydrate containing a higher valency main group metal atom and consists of a racemic mixture of  $\Lambda$ - and  $\Delta$ -trisoxalatoaluminium anions interspersed with  $\text{K}^+$  ions and hydrogen peroxide solvate molecules (Fig. 1). Hydrogen bonds link the two crystallographically independent hydrogen peroxide molecules into novel cyclic dimers, which use their two remaining H atoms to associate into chains with the *trans* O atoms (O10 and O11) of an oxalate ligand (Fig. 2). Each

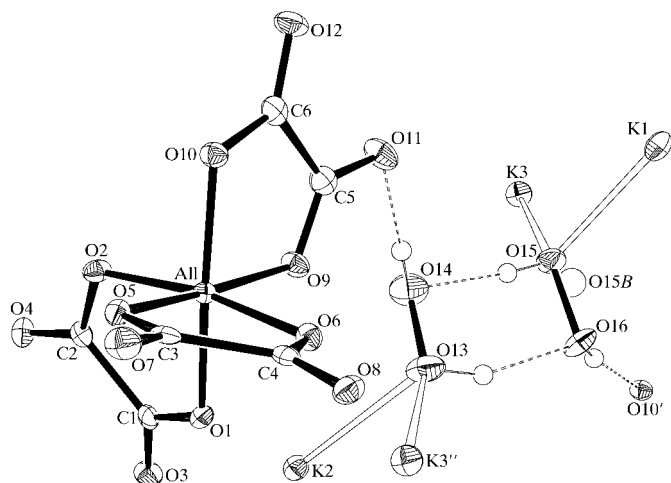
hydrogen peroxide molecule also uses one of its O atoms to coordinate to two  $\text{K}^+$  ions, with  $\text{K}\cdots\text{O}$  distances ranging from  $2.6620$  (9) to  $2.8380$  (7) Å (selected data are given in Tables 1 and 2). This arrangement leads to  $\text{H}-\text{O}-\text{O}-\text{H}$  torsion angles of  $119$  (1) and  $124$  (1)°, which correspond to low-energy conformations (Hunt *et al.*, 1965).

In 25% of their sites, hydrogen peroxide atoms O15 and O16 have been replaced by a single water O atom, O15B. Both hydrogen peroxide and water molecules share the same H atoms and, although the water geometry is somewhat distorted [ $\text{O}-\text{H} = 1.15$  (2) and  $1.34$  (2) Å, and  $\text{H}-\text{O}-\text{H} = 117$  (1)°], it clearly shows that a water molecule could replace hydrogen peroxide in the hydrogen-bonding scheme. Also, with distances of  $2.799$  (3) and  $2.881$  (3) Å, the water  $\text{K}\cdots\text{O}$  distances make a satisfactory substitute for the corresponding distances to hydrogen peroxide.

The non-solvate part of the structure is isostructural with the analogous trihydrate  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$ , which itself forms an isostructural series with the Cr (Taylor, 1978), Fe and V trihydrates (Gillard *et al.*, 1969). Two water molecules are located in peroxide sites O13 and O15, thereby maintaining the four  $\text{K}\cdots\text{O}$  bridging bonds, which range from  $2.683$  (6) to  $2.958$  (8) Å in the trihydrate. This leaves sufficient space for an additional water molecule, which coordinates to K3 at a distance of  $2.995$  (7) Å. Although disorder prevents the H atoms being located in the trihydrate, it is possible to deduce a hydrogen-bonding scheme from short non-bonded  $\text{O}\cdots\text{O}$  contacts (range  $2.753$ – $2.785$  Å). These indicate that the two hydrogen bonds to the oxalate ligand are maintained and that the only other hydrogen bond is between the additional water



**Figure 1**  
The unit cell of (I), viewed down the *a* axis.



**Figure 2**  
View of (I), showing the atomic labelling scheme (50% probability displacement ellipsoids). Only the boundary ellipse has been drawn for the 25% occupancy water molecule, O15B. The hydrogen peroxide environment in highlighted, with primes (') and double primes (") denoting symmetry codes  $(x - 1, \frac{1}{2} - y, z + \frac{1}{2})$  and  $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ , respectively.

molecule coordinated to K3 and that replacing O13. The complicated relationship between the title compound and its trihydrate contrasts with the more straightforward situation in the alkali metal oxalate monoperhydrates  $K_2(C_2O_4) \cdot H_2O_2$  and  $Rb_2(C_2O_4) \cdot H_2O_2$ . These are isostructural with their monohydrates; however, in the case of these monoperhydrates, a  $C_2$ -symmetric site can accommodate either a hydrogen peroxide or a water solvate molecule (Pedersen, 1967).

## Experimental

$K_3[Al(C_2O_4)_3] \cdot 3H_2O$  was prepared by reacting aluminium turnings (1 g) with KOH (6 g) in water (50 ml), heating the resulting solution and adding oxalic acid crystals (14 g). The solution was then filtered and cooled to room temperature before ethanol (50 ml) was added and the solution cooled to 273 K to induce crystallization. Crystals of (I) were prepared by dissolving the above hydrate in a 30% w/w aqueous  $H_2O_2$  solution and then evaporating to dryness at room temperature.

### Crystal data

$K_3[Al(C_2O_4)_3] \cdot 1.75H_2O_2 \cdot 0.25H_2O$	$D_x = 2.157 \text{ Mg m}^{-3}$
$M_r = 472.37$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 7200 reflections
$a = 7.6194 (2) \text{ \AA}$	$\theta = 1.0\text{--}27.5^\circ$
$b = 19.3531 (6) \text{ \AA}$	$\mu = 1.09 \text{ mm}^{-1}$
$c = 10.3668 (4) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 107.905 (1)^\circ$	Needle, colourless
$V = 1454.64 (8) \text{ \AA}^3$	$0.15 \times 0.15 \times 0.07 \text{ mm}$
$Z = 4$	

### Data collection

Nonius KappaCCD diffractometer	2390 reflections with $I > 2\sigma(I)$
$\omega$ and $\varphi$ scans	$R_{\text{int}} = 0.041$
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)	$\theta_{\text{max}} = 27.4^\circ$
$T_{\text{min}} = 0.849, T_{\text{max}} = 0.926$	$h = -8 \rightarrow 9$
7571 measured reflections	$k = -19 \rightarrow 25$
3256 independent reflections	$l = -11 \rightarrow 13$

**Table 1**  
Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

Al1—O1	1.9274 (7)	Al1—O6	1.8801 (5)
Al1—O2	1.8780 (5)	Al1—O9	1.8849 (7)
Al1—O5	1.9022 (7)	Al1—O10	1.9084 (7)
O2—Al1—O6	170.07 (3)	O9—Al1—O10	83.69 (3)
O6—Al1—O5	84.44 (3)	O2—Al1—O1	84.00 (3)
O9—Al1—O5	170.55 (3)		

**Table 2**  
Hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O13—H13 $\cdots$ O16	0.963 (17)	1.992 (17)	2.9139 (12)	159.5 (14)
O14—H14 $\cdots$ O11	1.183 (17)	1.527 (17)	2.6996 (11)	169.9 (12)
O15—H15 $\cdots$ O14	0.842 (14)	1.832 (15)	2.6633 (11)	169.4 (14)
O16—H16 $\cdots$ O10 <sup>i</sup>	0.881 (18)	1.858 (18)	2.7297 (12)	169.6 (14)

Symmetry code: (i)  $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$ .

**Table 3**  
Comparison of the hydrogen peroxide bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the alkali metal oxalates,  $M_2(C_2O_4) \cdot H_2O_2$ , with those in the title compound.

The hydrogen peroxide is bisected by an inversion point in the Li and Na salts, and by a twofold rotation axis in the K, Rb and  $NH_4$  compounds.

Cation(s)	O—H	O—O	O—O—H	H—O—O—H
Li <sup>+</sup> <sup>a</sup>	0.83 (10)	1.439 (15)	104 (5)	180
Na <sup>+</sup> <sup>ab</sup>	0.89 (5)	1.466 (9)	97 (3)	180
Na <sup>+</sup> <sup>ac*</sup>	1.0094 (9)	1.4670 (10)	99.95 (8)	180
K <sup>+</sup> <sup>ad*</sup>	1.0117 (5)	1.4578 (6)	100.69 (3)	101.6 (4)
Rb <sup>+</sup> <sup>ae*</sup>	0.99 (1)	1.509 (7)	100.8 (5)	—100 (1)
Rb <sup>+</sup> <sup>af*</sup>	0.972 (7)	1.487 (4)	101.8 (4)	104.5 (5)
$NH_4^+ag$	0.83 (2)	1.452 (2)	99 (1)	121 (3)
Al <sup>3+</sup> /K <sup>+</sup> <sup>ah</sup>	0.96 (2), 1.18 (2) <sup>i</sup>	1.4415 (9)	91 (1), 101 (1)	119 (1)
Al <sup>3+</sup> /K <sup>+</sup> <sup>ah</sup> (disorder)	0.84 (1), 0.88 (2)	1.4675 (12)	96 (1), 86 (1) <sup>j</sup>	124 (1)

Notes: (a) Pedersen (1969); (b) Pedersen & Pedersen (1964); (c) Pedersen & Kvick (1989); (d) Pedersen & Kvick (1990); (e) Adams *et al.* (1980a); (f) Adams *et al.* (1980b); (g) Pedersen (1972); (h) this work; (i) the H atom had a fixed vibrational amplitude; (j) probably influenced by the close proximity of partial water atom O15B; (\*) neutrons used.

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0101P)^2 + 2.2968P]$
$R(F) = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.088$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
3256 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$
256 parameters	Extinction correction: SHELXL97
All H-atom parameters refined	Extinction coefficient: 0.00282 (13)

Although atom H14 appeared in a chemically reasonable position in the  $\Delta F$  map, its displacement parameter expanded on least-squares refinement and the atom moved away from O14 to encompass diffuse electron density on the nearby oxalate O atom to which it is hydrogen bonded. This problem was resolved by fixing the vibrational amplitude of H14 to the average value of the other three H atoms, whilst leaving its positional parameters to refine freely. The 25% occupancy water H atoms attached to O15B were assumed to coincide with hydrogen peroxide atoms H15 and H16, although it was envisaged that their actual site will be slightly shifted so that hydrogen bonding is maintained and the water geometry is more typical.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1158). Services for accessing these data are described at the back of the journal.

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